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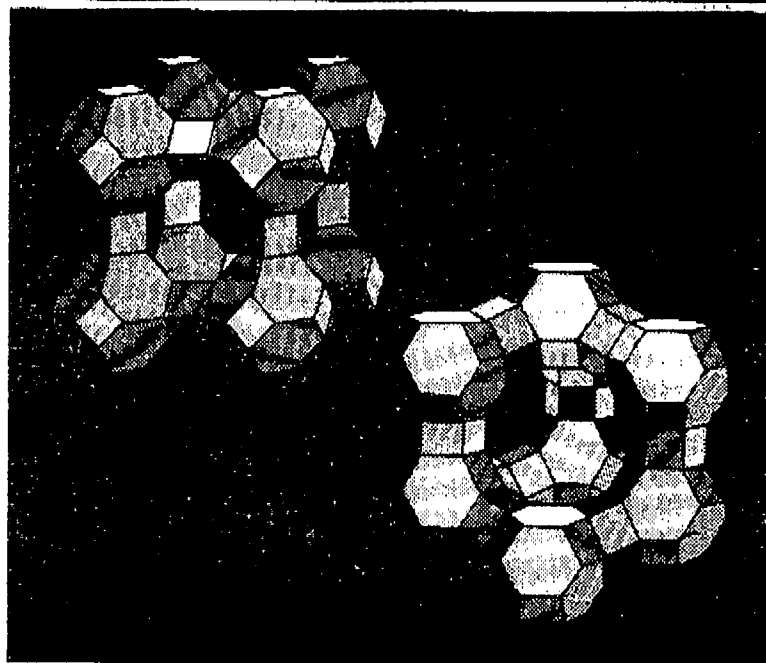*Document Number:*

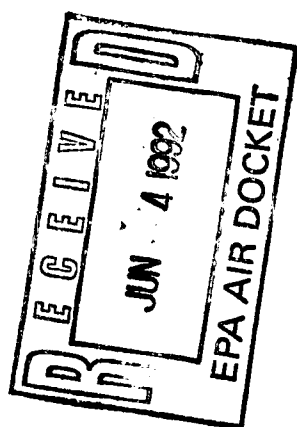## 205) IV-B-12

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Heterogeneous Catalysis

Principles and Applications

SECOND EDITION

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and NO_x must therefore be removed by reduction to N_2. More than one type of catalyst configuration may be utilized, depending on engine characteristics and other design factors. The central problem is that a vehicle does not run at steady-state conditions.

For many cases it appears that the concentrations of hydrocarbons, CO, and NO_x can be reduced to the desired level simultaneously in a single catalyst unit operated in a narrow range around the stoichiometric air/fuel ratio. This requires precise control of the fuel-air mixture fed to the automobile engine at all operating conditions, so as to operate the catalyst in the narrow "window" of composition in which this degree of pollution control can be achieved. Generally an oxygen sensor in the engine exhaust stream with a feedback control system, is required. This type of unit is termed a *three-way catalyst* because all three pollutants are removed simultaneouly.

The most active catalyst is platinum, but some of the NO_x is reduced to NH_3 instead of N_2, which is not desired. The most effective catalyst for conversion of NO_x to N_2 appears to be one in which some rhodium is added to the platinum. However there is no primary production of rhodium anywhere in the world; it is produced as a byproduct of production of platinum and palladium, the ratio of rhodium to platinum in South African ores, for example, being about 0.06 to 0.04. Therefore the optimum catalyst composition will be markedly influenced by market economics which set the price of a byproduct of strictly limited availability. Catalyst compositions containing ruthenium in various forms appear to be effective for conversion of NO_x to N_2. However these may be converted to ruthenium oxides under oxidizing conditions, as might occur occasionally during engine operation. These oxides are volatile and poisonous. Ruthenium is likewise produced only as a byproduct, but in South African ores mined primarily for platinum it is present in greater amounts than rhodium.

In a number of car applications it may be necessary to provide a second oxidation catalyst following the three-way catalyst, additional air being supplied between the two catalyst beds.

Information on automobile catalysts is extensive, widely scattered, heavily patented, and highly proprietary, and much of it is of rather short half-life because of the rapidly moving state of affairs. The papers in a symposium edited by McEvoy (1975) show some of the complexities involved in attempting to reach an overall optimum solution. A review by Dwyer (1972) treats some of the earlier catalysts considered. A review by Shelef (1975) considers NO_x-removal reactions in great detail. Wei (1975) reviews automobile catalysts with particular attention to kinetics and reactor engineering. Resistance to sintering and to agglomeration of precious metal crystallites is of prime importance, a subject discussed in Chaps. 4 and 6. Poisoning of automobile catalysts is reviewed by Shelef et al. (1978).

8.13 CATALYTIC COMBUSTION

There are a large variety of uses of catalytic combustion beyond that in automobiles, and some have been applied for many years. Low concentrations of hydrocarbon and organic pollutants in air, as from painting operations, can thus be eliminated. In some cases a gaseous stream may contain CO and hydrocarbons in sufficiently high concen-

iridium are also recovered as byproducts of refining gold from certain South African ores. This concentrate is termed *osmiridium* and typically is one-third Os, one-third Ir, and about one-sixth Pt.

In the United States little Pt is used in jewelry. About one-third of the total Pt plus Pd is used for motor-vehicle catalysts, and about one-quarter in chemical and petroleum processing. The primary producers usually set a *producer price* for long-term customers under contract, which is changed with supply and demand. Spot prices may fluctuate greatly and relatively quickly both above and below the producer price, especially for the precious metals other than platinum and palladium. The production of these is essentially inflexible, so slight changes in demand can markedly affect price. The market prices for platinum and palladium also tend to move with current prices for gold since they are also purchased as an investment or speculative vehicle. The producer price for platinum in the United States during 1977 and 1978 varied between $162 and $300 per troy ounce and spot prices on the free market varied between about $144 and $392 per troy ounce, although market fluctuations during this period were unusually great. The average producer price in 1978 was $237 per troy ounce for platinum and $71 per troy ounce for palladium. Approximate prices in 1978, in dollars per troy ounce, for the other platinum-group metals were about: Ru, 60; Rh, 500; Ir, 250; Os, 150. In comparison, in recent years market prices for such base metal catalysts as Ni, Cr, Mo, and Co have been in the range of $2 to $20 per pound of metal. The average 1978 price for rhenium, used in reforming catalysts, was about $350 per pound.

Since platinum-group metals are expensive, the loading used in auto catalysts is the minimum necessary to meet standards. This works out to an amount of platinum plus palladium in the range typically of about 1 to 2 g per catalyst unit, to meet federal standards for 1980 models. The catalysts may be somewhat poisoned by SO_x in the exhaust gases, but the poisoning appears to be reversible; that is, SO_x is adsorbed at lower temperatures and desorbed at higher temperatures.

The catalyst temperature is in the range of 400 to 600°C during normal operation, but may rise several hundred degrees above this under extreme driving conditions or with engine malfunction. The reaction is highly mass-transfer-limited after the engine reaches operating temperature, and the most effective use of the noble metal catalyst is to deposit it in a relatively thin layer near the outside catalyst surface. Poisons will generally accumulate on the outermost surface of the porous support, so optimally the noble metal layer should probably be displaced slightly into the interior to prolong catalyst life. This is sometimes termed an *eggshell*-type deposit. A further complication is that the rate of CO oxidation on platinum is an inverse function of CO concentration. In a diffusion-limited reaction on a catalyst with uniform Pt distribution, the local rate will *increase* with depth of penetration up to a certain percent conversion (Wei and Becker, 1975). This is unlike the usual case in which reaction rate is decreased by a diffusion limitation.

8.12.1 NO_x Removal Catalyst

The more stringent limitations set for NO_x emissions (NO and NO_2) from automobiles for 1981 and later years requires in most cases a suitable catalyst for this purpose. No catalysts of sufficient activity for decomposition of NO_x are known,

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honeycomb monolith is used consisting of a block of parallel, nonintersecting channels. (See Figs. 4.13, 4.14, and 4.15.) This is composed of cordierite, a magnesium aluminum silicate, $Mg_2Al_3(AlSi_5O_{18})$, which has a low coefficient of thermal expansion and is mechanically strong. The monolith surfaces are covered with a wash coat of alumina, and the noble metal is impregnated onto this. The open cross-sectional area is typically 70 percent or so of the total, and the number of cells per square inch ranges from 200 to 400 (31 to 62 cells per square centimeter), the corresponding wall thicknesses being, for example, 10 or 6 mils (0.25 or 0.15 mm), respectively. The material of higher cell count is somewhat more expensive to fabricate but allows a smaller unit to be utilized. The less the mass, the more rapidly it becomes heated up to the ignition temperature. For the same reason, specially fabricated alumina pellets of low mass are used in the packed-bed configuration.

Platinum is more active for oxidation of paraffin hydrocarbons, palladium for oxidation of CO and possibly unsaturated hydrocarbons. In an oxygen atmosphere, platinum on alumina sinters more readily than does palladium (Klimisch et al., 1975), but platinum is more resistant to lead poisoning than is palladium. Under most oxidizing conditions palladium probably exists in the form of PdO, which is more active for oxidation than the metallic form. Platinum is more active as the metal, on which oxygen is chemisorbed.

Platinum and palladium are found together in ores located predominantly in the USSR and South Africa. Their individual price in the marketplace is dictated by the relative demand for the two metals compared to the ratio in which they occur in nature. The demand for platinum in the Western world was about 2,500,000 troy oz per year as of 1978,[2] of which about one-half was for use in jewelry, especially in Japan. Use in automobile catalysts was the next largest demand, making up about one-third of the total. Over the past several years about two-thirds of the supply has come from South Africa, about 5 to 10 percent as a byproduct of nickel refining from the Inco operations at Sudbury, Canada, and almost all of the remainder from the USSR. The supply from the USSR is irregular but has averaged in the neighborhood of 600,000 troy oz per year over the last several years. This is probably a byproduct of nickel operations, and the ratio of palladium to platinum appears to be much higher than that in South African ores. The amount from the Inco operations depends on the primary demand for nickel, whereas the South African ores are mined for primary production of platinum and palladium; other precious metals and nickel are produced as by-products. The largest demand for palladium is in the electronics industry for use largely in conductive inks and protective coatings.

The world production of the *platinum-group* metals (Ru, Rh, Pd, Os, Ir, Pt) was about 6,000,000 troy oz per year as of 1978, of which about one-third was used in the United States. In South Africa the ores are mined from what is known as the Merensky Reef and the platinum-group metal content is about 0.2 troy oz per ton of ore. Their relative weight proportions are about as follows: Pt, 1: Pd, 0.6 to 0.4; Ru, 0.15 to 0.07; Rh, 0.06 to 0.04; Ir, 0.02 to 0.01; Os ~ 0.002. Some osmium and

[2]Precious metals are sold by the troy ounce (1 troy oz = 31.1 g), but the price per gram-atom may be a more meaningful unit in catalysis in cases in which one element may be substituted for another. Historically, platinum has sold at a higher price per unit weight than palladium, but since palladium has an atomic weight of 106 versus 195 for platinum, the economies in favor of palladium are greater than a casual observation might imply.

comes first. The federal standard for NO_x was 2.0 g per mile for cars of model years through 1980, which was generally met by engine modifications. However, the level of 1.0 g per mile set for 1981-model cars necessitates the use of a catalyst system of a different type than that introduced for 1975-model cars, which was an oxidation catalyst only. (See Sec. 8.12.1.)

The catalyst application to automobiles is unique. It was the first large-scale use of a catalyst in a product for consumers, supposed to perform for at least 5 years without attention by technically trained people, or indeed by anyone at all. Nearly complete oxidation is required of an intermittent gaseous stream whose temperature, composition, and flow rate varies in an erratic pattern and which may contain traces of any of a wide variety of catalyst poisons from fuel additives, lubricating oil, and corrosion.[1] Further the unit must be compact because of stringent volume limitations, and the thermal mass must be as low as possible so the catalyst can reach ignition temperature rapidly, whereupon the emission control starts. The catalyst bed must operate at an extremely low pressure drop in order to minimize power loss from the engine. The sums of money expended for research and development of this single product stretch into the hundreds of millions of dollars and probably exceed that for any other single catalyst application. To date catalyst units in automobiles have been remarkably free of consumer complaint, probably in part because as yet their performance is rarely evaluated after the car has been acquired by the user. This situation will probably change in the future.

In spite of intensive study no catalyst composition has yet been developed that exhibits the requisite activity and durability when the fuel contains lead alkyls, commonly added to raise the octane number of gasoline (Chap. 9), or phosphorus compounds. Hence nonleaded gasoline must be used. Various base metal oxides exhibit good catalytic activity for oxidation, two of the most active being cobalt oxide and copper chromite. However they may be insufficiently resistant to sintering at high temperatures to meet durability standards, and they are less active than noble metal catalysts at the low temperatures of the engine warm-up period. They also may be more susceptible to poisoning from SO_x in the exhaust gases. Some base oxide compositions may also deteriorate when subjected alternately to a net oxidizing and net reducing environment.

The catalysts used for oxidation of CO and hydrocarbons as of 1980 are in all cases platinum or platinum plus a little palladium. These are more active and more durable than base oxide systems. Either of two catalyst configurations is used. In one the noble metal is supported on alumina beads held in a thin layer in a rather flat pancakelike alloy steel container. The gases flow down through the layer. In the second a

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[1] The potential cumulative effect of even traces of poisons in the reacting gases in contact with a catalyst can be vividly seen in this application. On average an automobile burns its weight in fuel every year. With a 1000-kg car, over a 5-year period about 5000 kg of fuel would be consumed at an air/fuel weight ratio of about 14.5/1. About 72,500 kg of air with the products of combustion will contact the catalyst. If the usual leaded gasoline containing 3 g of lead per gallon were to be used, 5 kg of lead would pass through a catalyst on which about 1 to 2 g of precious metal is supported. Even with "lead-free" gasoline, which is specified as containing no more than 0.05 g of lead per gallon, over a 5-year period this amounts to about 80 g. With a sulfur content of about 100 ppm in gasoline, which is set as the desirable standard for fuel to be used with a catalyst, about 9 kg of sulfur dioxide will contact the catalyst.

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of the reaction occurs in a short portion of the tube and largely under mass-transfer-controlling conditions; the first portion of the tube is required for heat-up and the last for cooling. B~cause of the large difference in molecular weight between H_2 and the other species present and the large temperature gradient between wall and gas at the exit, Koberstein calculates that considerable separation of the products occurs by thermal diffusion.

A higher concentration of HCN is produced in this process than in the Andrussow process, which lowers subsequent costs of purification; but the process is sensitive to operate, and it seems to be economic only in a small installation and where natural gas is expensive.

~>me HCN is also produced as a byproduct of manufacture of acrylonitrile. HCN is u   . primarily to make adiponitrile by reaction with butadiene (for nylon 66) and methyl methacrylate via reaction with acetone and esterification with methanol. Methyl methacrylate is polymerized to form transparent plastics such as Lucite and Plexiglas and protective coatings. Some HCN is also used to make chelating agents.

8.12 CONTROL OF AUTOMOBILE-ENGINE EMISSIONS

The exhaust from the internal-combustion engine of an automobile contains small concentrations of hydrocarbons and CO from incomplete combustion of fuel, and of nitrogen oxides, NO_x, from nitrogen fixation at the high temperature of combustion. These contaminants are a major contributor to air pollution and one of particular concern in urban areas.

Federal legislation in the United States, which went into effect for 1975-model cars, established maximum permissible emission levels for automobiles in terms of the emissions of three pollutants, expressed as grams of hydrocarbons, CO, and NO_x per mile traveled. The concentrations are averaged in a detailed test procedure that simulates representative modes of operation of an automobile during warm-up and driving after the engine reaches normal operating temperature. Pollutant emissions can be reduced to some extent by internal-combustion engine modifications and by precise control of fuel/air ratio. However with a few exceptions, mostly small cars, the specified emission levels for CO and hydrocarbons can be reached only by use of a catalyst for oxidation of these species in the exhaust to CO_2 and H_2O. The situation has been complicated in the United States by the fact that a schedule of gradually lowering maximum allowable pollutant emission levels has been established by law and then modified and/or postponed, as the technical problems and costs to be borne by the public became clearer. For the model years of 1981 and some time into the future the maximum allowable levels (in grams per mile) have been set as 0.41 hydrocarbons, 3.4 CO, and 1.0 NO_x. A level of 0.40 NO_x called for in the original legislation has subsequently been recognized as being very difficult to meet within reasonable economic constraints and remains as a research goal.

Individual states may set more stringent levels than those called for by federal law. For a period those in California were more stringent than the federal standards, but that is not the case for 1981-model cars. Legally, the catalyst system in the new vehicle must continue to meet specified standards for 50,000 mi or 5 years, whichever